Irreducible Cartesian and spherical tensors

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Physical properties of matter represent the coupling action of matter between influences exerted and effects obtained (VOIGT–1928). However not all quantities entering in effect–influence relations are physical properties of matter. In this respect one distinguishes between **field quantities** and **matter quantities**. While matter quantities are in themselves consequences of the intimate structure and cohesion of matter, field quantities simply represent field induced in matter by external causes: typical examples are susceptibility (matter quantity) and Lorentz field (field quantity).

Generally more than one number is required to specify a physical property at a point in a material system: when this occurs, the property is called **anisotropic** since the property depends on direction. When only one number is necessary in any material system, the property does not depend on direction and is called scalar. The numbers specifying a scalar property at a given point transforms as a tensor of **order zero** of polar or axial nature. The numbers specifying anisotropic properties frequently transforms as of polar and axial tensors of **order greater then one**.

Macroscopic space symmetry is responsible for the reduction of independent matter tensor components in symmetrical material systems. Matter tensors component must be invariant under the existing symmetry: **The number of independent components of a matter tensor in a system of a given symmetry is invariant under coordinate transformation**.

$$k = \frac{1}{N} \sum_{g \in G} \chi^m(g)\, \chi(g) \tag{1}$$

Moreover it is convenient to decompose a tensor **into sets that transform irreducibly**, both with respect to the rotation group $\mathbf{O}(3)$ and the permutation group $\mathbf{S}_i$ of its indices.

$$G_p = G \otimes P \tag{2}$$

With respect to the three–dimensional rotation group, a tensor $T = T^{1\ldots1}$ of order l and with each of its ranks equal to one is defined by 3^l components. The Cartesian components $(T_{i_1\ldots i_l};\, i_k = x, y, z)$ and the reducible spherical components $(T^{1\ldots1}_{m_1\ldots m_l};\, m_k = 1,\, 0 - 1$ are characterized by their law of transformation:

$$T_{i_1\ldots i_l} = \sum_{i'_1\ldots i'_l} T_{i'_1\ldots i'_l} \prod_{k=1}^{l} R^{i'_k}_{i_k} \tag{3}$$

$$T^{1\ldots1}_{m_1\ldots m_l} = \sum_{m'_1\ldots m'_l} T^{1\ldots\ldots1}_{m'_1\ldots m_l{}'} \prod_{k=1}^{l} \mathcal{D}^{1}_{m'_k\, m_k}(R) \tag{4}$$

where $\mathcal{D}^{1}_{m'_k\, m_k}(R)$ is the irreducible rotation matrix.

A rank–l Cartesian tensor $T_{(l)}$ has 3^l components; an irreducible rank–l tensor is labeled by its weight j. It has (2j+1) components which subtend a weight–j irreducible representation of the rotation group $\mathbf{O}(3)$. If several linearly independent irreducible tensors of the same weight j appear in the reduction of $T_{(l)}$ they can be distinguished by an additional superscript τ, called the seniority index, so that the most general form of a tensor reduction is

$$T_{(l)} = \sum_{\oplus \tau, j} T_{(l)}^{(\tau, j)} \tag{5}$$

This equation is often refered to as the reduction spectrum of $T_{(l)}$.

Any tensor $T^{1...1}$ of order l greater than one can be decomposed into irreducible tensors $T = T^{(1...1,\lambda\,\alpha)\,j}$ of integer rank j $(0 \leq j \leq l)$, and characterized by a coupling scheme specified by l-2 intermediate couplings $\lambda = (\lambda_k;\, k = 1, ..., l-2)$ and their order symbolically denoted by α. One then defines a transformation

$$T_m^{(1...1,\lambda\,\alpha)\,j} = \sum_{i_1...i_l} T_{i_1...i_l} \; < i_1...i_l|\lambda\,\alpha\,, j\,m > \tag{6}$$

Attention is now focused on the coupling to the highest value l of j. By definition, an irreducible Cartesian tensor, also said to in natural form (Coope et al 1965), is a tensor of order l with l ranks one, such that all its irreducible tensors vanish except the one with the highest rank l, denoted by $(T_l)^l$. Such tensor is completely symmetric and traceless.

$$\alpha_{l_1\,1}^{\beta\,m_1} = \sum_{j_1\phi} C(l_1\,1\,j_1;\beta\,m_1\,\phi)\;\alpha_{j_1\phi}^{(l_1\,1)} \tag{7}$$

$$\Delta A_{K\,M}^{(1\,,1)} = \sum_{m_1\,m_2} C(1\,1\,K;m_1\,m_2\,M)\;\Delta A_{1\;\;1}^{m_1\,m_2} \tag{8}$$

$$\beta_{l_i\;\;1\;\;1}^{m_i m_1 m_2} = \sum_{a,\xi,J_i,M_i} C(11a;m_2 m_1 \xi)\;\;C(a l_i J_i;\xi m_i M_i)$$
$$\beta_{J_i M_i}[(11)a l_i] \tag{9}$$

Dipole moment

$$Q_1^0 = \mu_z \tag{10}$$

$$Q_1^{\pm 1} = \mp \frac{(\mu_x \pm i\,\mu_y)}{\sqrt{2}} \tag{11}$$

Quadrupole moment

$$Q_2^0 = \Theta_{zz} \tag{12}$$

$$Q_2^{\pm 1} = \mp \sqrt{\frac{2}{3}}\,(\Theta_{zx} \mp i\,\Theta_{yz}) \tag{13}$$

$$Q_2^{\pm 2} = \frac{1}{\sqrt{6}}\,(\Theta_{xx} - \Theta_{yy} \pm 2\,i\,\Theta_{xy}) \tag{14}$$

Octopole moment

$$Q_3^0 = \Omega_{zzz} \tag{15}$$

$$Q_3^{\pm 1} = \mp \sqrt{\frac{3}{4}} \left(\Omega_{zzx} \pm i\, \Omega_{zzy} \right) \tag{16}$$

$$Q_3^{\pm 2} = \sqrt{\frac{3}{10}} \left(\Omega_{zxx} - \Omega_{zyy} \pm 2\, i\, \Omega_{xyz} \right) \tag{17}$$

$$Q_3^{\pm 3} = \mp \frac{1}{\sqrt{20}} \left(\Omega_{xxx} \pm 3\, i\, \Omega_{xxy} - 3\, \Omega_{xyy} \mp i\, \Omega_{yyy} \right) \tag{18}$$

For nitrogen (a $D_{\infty h}$ symmetry molecule) in its principal axes reference frame, reducible spherical dipole–octopole $\bar{\alpha}_{1\ \ 3}^{m_1\, m_2}$ and the dipole–dipole–quadrupole $\bar{\beta}_{1\ \ 1\ \ 2}^{m_1\, m_2\, m_3}$ tensors have the following non-zero components which are related with their Cartesian counterparts as follows:

a) for the dipole–octopole tensor, assuming the Cartesian components $E_{z,zzz}$ and $E_{x,xxx}$ as mutually independent

$$\bar{\alpha}_{1\,3}^{0\,0} = E_{z,zzz} \tag{19}$$

$$\bar{\alpha}_{1\ \ 3}^{1\,-1} = \bar{\alpha}_{1\ \ 3}^{-1\,1} = \sqrt{\frac{8}{3}}\, E_{x,xxx} \tag{20}$$

b) for the dipole–dipole–quadrupole tensor, assuming the Cartesian components $B_{xx,xx}, B_{zz,zz}, B_{xz,xz}$ and $B_{xx,zz}$ as mutually independent

$$\bar{\beta}^{0\,0\,0}_{1\,1\,2} = B_{zz,zz} \tag{21}$$

$$\bar{\beta}^{\pm 1\,\mp 1\,0}_{1\;\;1\;\;2} = -\,B_{xx,zz} \tag{22}$$

$$\bar{\beta}^{0\,\pm 1\,\mp 1}_{1\;\;1\;\;2} = \bar{\beta}^{\pm 1\,0\,\mp 1}_{1\,1\;\;2} = -\,\frac{2}{\sqrt{3}}\,B_{xz,xz} \tag{23}$$

$$\bar{\beta}^{\pm 1\,\pm 1\,\mp 2}_{1\;\;1\;\;2} = \frac{2}{\sqrt{6}}\left(2\,B_{xx,xx} + B_{xx,zz}\right) \tag{24}$$

The irreducible polarizability tensors are constructed from — by

standard coupling methods:

$$A^{(13)}_{j\,0} = \sum_m C^{j\,0}_{1\,m\;3\,-m}\,\bar{\alpha}^{m\,-m}_{1\,3} \tag{25}$$

$$B_{j\,0}((11)l,2) = \sum_{m_1,m_2} C^{l\,-(m_1+m_2)}_{1\,m_1\;1\,m_2}\,C^{j\,0}_{l\,-(m_1+m_2)\;2\;m_1+m_2}\,\bar{\beta}^{m_1\;m_2\;-(m_1+m_2)}_{1\quad 1\quad 2} \tag{26}$$

where $C^{j\,m_3}_{j_1\,m_1\;j_2\,m_2}$ stands for the Clebsch-Gordan coefficient. The linear combinations (25) and (26) give the mutually independent components and of, respectively, the irreducible spherical multipolar polarizability dipole-octopole (**E**) and dipole–dipole–quadrupole (**B**) tensors.

For second–rank tensors the reduction reads

$$T_{ij} = T_{ij}^{(0)} + T_{ij}^{(1)} + T_{ij}^{(2)} \tag{27}$$

where

$$\begin{aligned} T_{ij}^{(0)} &= \left(\frac{1}{3}\,T_{kk}\right)\,\delta_{ij}; \quad T_{ij}^{(1)} = \frac{1}{2}\,(T_{ij} - T_{ji}) \\ T_{ij}^{(2)} &= \frac{1}{2}\,(T_{ij} + T_{ji}) - \left(\frac{1}{3}\,T_{kk}\right)\,\delta_{ij} \end{aligned} \tag{28}$$

A tensor of rank 3 symmetric in the permutation of two of its indices can be formed by multiplication of a symmetric rank–2 tensor and a rank–1 tensor and its reduction spectrum is

$$1 \otimes (0 \oplus 2) = (1 \otimes 0) \oplus (1 \otimes 2) = (1) \oplus (1 \oplus 2 \oplus 3) \tag{29}$$

For a fully symmetric rank–3 tensor the reduction spectrum is $1 \oplus 3$. In the general case a third–rank tensor has $3^3 = 27$ independent components. It is a sum of one pseudo–scalar (j=0), three vectors (j=1), two pseudo–deviators (j=2) and one septor (j=3) ($27 = 1 + 3 \times 3 + 2 \times 5 + 7$).

A rank–4 tensor has $3^4 = 81$ components. According to table 1 it is the direct sum of three scalars (j = 0 , 2 J+1 = 1), six pseudo–vectors (J = 1, 2 J + 1 = 3), six deviators (J =2 , 2 J+1 = 5), three pseudo–septors (J=3 , 2 J+ 1 = 7) and one nonor (J=4 , 2 J+ 1 =9)

$$3 \times 1 + 6 \times 3 + 6 \times 5 + 3 \times 7 + 1 \times 9 = 81 \qquad (30)$$

A number of physical properties are described by rank–4 tensors; some are listed in table 1 with their intrinsic symmetry and reduction spectrum.

THE DUAL PICTURE–CARTESIAN AND SPHERICAL TENSORS

For low–rank tensors (l=0, 1) the transformation to spherical tensors is straightforward and unambiguous, since the tensors are irreducible (3^l=2 j+1). In the case of scalars l=j=0 the connection is just identity. Vector quantities l=j=1 we can expand either in the Cartesian basis $|i>$ with i=x, y, z or in a spherical basis $|1\,\mu>$ with μ=+1, 0, -1. The unitary transformation $<i\,|1\,\mu>$ between the two basis is

$$\begin{bmatrix} -\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ -\frac{i}{\sqrt{2}} & 0 & -\frac{i}{\sqrt{2}} \\ 0 & 1 & 0 \end{bmatrix} \tag{31}$$

i.e. for the component of a tensor T

$$T_1 = -\frac{(T_x + i\,T_y)}{\sqrt{2}} \quad T_0 = T_z \quad T_{-1} = \frac{(T_x - i\,T_y)}{\sqrt{2}} \tag{32}$$

In the case of higher-rank tensors, the correspondence is less obvious. Starting from a rank–n tensor $T_{i_1,i_2\ldots i_n}$ one first changes the Cartesian coordinates into spherical coordinates through a product of n unitary transformations $< i\,|1\,\mu >$. This results in a reducible tensor $T_{\mu_1,\mu_2\ldots\mu_n}$, which is reduced by use of the well–known properties of the Clebsch–Gordan and Racah 3n–j coefficients to give the irreducible tensors $T_m^{(\tau\,j)}$ (the seniority index τ distinguishes among various spherical tensors with identical weight appearing in the reduction of T.)

The transformation from Cartesian tensors $T_{(i)}$ to irreducible spherical tensors $T_m^{(\tau\, j)}$ is a unitary transformation

$$T_{(i)} = < (i)|\tau\, j\, m > T_m^{(\tau\, j)}; \quad T_m^{(\tau\, j)} = < \tau\, j\, m|(i) > T_{(i)} \quad (33)$$

where (i) stands for a whole set of Cartesian indices. The transformation satisfies the usual unitary properties

$$\begin{aligned} &< \tau\, j\, m|(i) >< (i)|\tau^{'}\, j^{'}\, m^{'} > = \delta_{\tau\tau'}\, \delta_{j\, j'}\, \delta_{m\, m'} \\ &< (i)|\tau\, j\, m >< \tau\, j\, m|(i^{'}) > = \delta_{(i)\,(i')} \\ &< \tau\, j\, m|(i) > = < (i)|\tau\, j\, m >^{*} \end{aligned} \quad (34)$$

The $< \tau\, j\, m|(i) >$ coefficient is build up by a product of transformations from the Cartesian basis to a spherical one

$$T_{\mu_1,\mu_2...\mu_n} = < 1\, \mu_1|i_1 > \\ < 1\, \mu_2|i_2 > ... < 1\, \mu_n|i_n > \; T_{i_1,i_2...i_n} \tag{35}$$

and then by reducing the spherical tensor $T_{(\mu)}$ by use of $< \tau\, j\, m|\mu_1\, \mu_2...\mu_n >$ coefficients expressible in terms of $3n - j$ symbols, so that the overall transformation is, in a condensed form

$$T_{\mu_1,\mu_2...\mu_n} = < \tau\, j\, m|\mu_1\, \mu_2...\mu_n > < 1\, \mu_1|i_1 > \\ < 1\, \mu_2|i_2 > ... < 1\, \mu_n|i_n > \; T_{i_1,i_2...i_n} \tag{36}$$

LINEAR LIGHT SCATTERING

$$
\begin{aligned}
I^{\omega}_{ij} &= A^{\omega}\, N \left\langle m_i m^*_j \right\rangle \\
I^{\omega}_{\mathbf{n}} &= A^{\omega}\, N \left\langle n^*_i\, n_j\, m_i\, m^*_j \right\rangle \\
&= A^{\omega}\, N \left\langle \left(n^*_i\ A_{ik}\, e_k\right) \left(n_j\, A_{jp}\, e^*_p\right) \right\rangle E^2 \\
I^{\omega}_{\mathbf{n}} &= A^{\omega}\, N \left\langle (\mathbf{W} : \mathbf{A})\ (\mathbf{W} : \mathbf{A}) \right\rangle E^2
\end{aligned}
\tag{37}
$$

$$
I^{\omega}_{\mathbf{n}} = A^{\omega} N \frac{1}{2j+1} \left(\mathbf{W}^{(j)} \bullet \mathbf{W}^{(j)}\right) \left\langle \left(\mathbf{A}^{(j)} \bullet \mathbf{A}^{(j)}\right) \right\rangle E^2 \tag{38}
$$

$$
W_{ij} = n^*_i\, e_j \tag{39}
$$

isotropic scattering

$$\phi_{00} = \frac{1}{3} W_{kk} \, \delta_{ij} \, \frac{1}{3} W^*_{pp} \, \delta_{ij} = \frac{W_{kk} \, W^*_{pp}}{3} = \frac{(\mathbf{n}^* \cdot \mathbf{e}) \, (\mathbf{n} \cdot \mathbf{e}^*)}{3} \tag{40}$$

$$F_{00} = \frac{1}{3} A_{kk} \, \delta_{ij} \, \frac{1}{3} A^*_{pp} \, \delta_{ij} = \frac{A_{kk} \, A^*_{pp}}{3} = 3 \, A^2 \tag{41}$$

antisymmetric scattering

$$\begin{aligned}\phi_{11} &= \frac{1}{3}\,\frac{1}{2}\,(W_{ij} - W_{ji})\;\frac{1}{2}\,(W^*_{ij} - W^*_{ji}) \\ &= \frac{1}{6}\,\left[1 - (\mathbf{n}^* \cdot \mathbf{e}^*)\,(\mathbf{n} \cdot \mathbf{e})\right] \end{aligned} \tag{42}$$

$$\begin{aligned}F_{11} &= \frac{1}{2}\,(A_{ij} - A_{ji})\;\frac{1}{2}\,(A^*_{ij} - A^*_{ji}) \\ &= \frac{1}{2}\,\left(A_{ij}\,A^*_{ij} - A_{ij}\,A^*_{ji}\right) \end{aligned} \tag{43}$$

anisotropic (depolarized) scattering

$$\begin{aligned}
\phi_{22} &= \frac{1}{5}\left\{\left[\frac{1}{2}\left(W_{ij} + W_{ji}\right) - \frac{1}{3}W^*_{kk}\,\delta_{ij}\right]\right. \\
&\qquad \left.\left[\frac{1}{2}\left(W^*_{ij} + W^*_{ji}\right) - \frac{1}{3}W^*_{kk}\,\delta_{ij}\right]\right\} \\
&= \frac{1}{10}\left[1 + \left(\mathbf{n}^*\cdot\mathbf{e}^*\right)\left(\mathbf{n}\cdot\mathbf{e}\right)\right] - \frac{\left(\mathbf{n}^*\cdot\mathbf{e}\right)\left(\mathbf{n}\cdot\mathbf{e}^*\right)}{15} \qquad (44)
\end{aligned}$$

$$F_{22} = \frac{3\left(A_{ij}\,A^*_{ij} + A_{ij}\,A_{ji}\right) - 2A_{ii}\,A^*_{jj}}{6} \qquad (45)$$

for real **n** and **e**

$$\phi_{22} = \frac{1}{30}\left[3 + (\mathbf{n}\cdot\mathbf{e})^2\right] \tag{46}$$

for real and symmetric A_{ij}

$$F_{22} = \frac{3\,A_{ij}\,A_{ij} - A_{ii}\,A_{jj}}{3} \tag{47}$$

Within principal axis of a molecule only diagonal elements A_{xx}, A_{yy} and A_{zz} of **A** are different from zero, then

$$F_{22} = \frac{(A_{xx} - A_{yy})^2 + (A_{xx} - A_{zz})^2 + (A_{yy} - A_{zz})^2}{3}$$

$$\overbrace{=}^{STM} \frac{2\,(A_{zz} - A_{xx})^2}{3} \tag{48}$$

$$I_{iso} = \frac{1}{3}\,3\,A^2 = A^2 \tag{49}$$

$$I_{dep\,(VH)}(\mathbf{n} \perp \mathbf{e}) = \frac{1}{10}\,\frac{2\beta^2}{3} = \frac{1}{15}\,\beta^2 \tag{50}$$

THE POLARIZATION STATE OF HYPER-RAYLEIGH SCATTERED LIGHT

$$\left(\mathbf{W}^{(s_1,j_1)} \odot \mathbf{W}^{(s_2,j_2)*}\right) = W_{IJK}^{(s,J)} \; W_{IJK}^{(s,J)*} \tag{51}$$

$$\left(\boldsymbol{\beta}^{(s,J)} \odot \boldsymbol{\beta}^{(s,J)*}\right) = \beta_{ijk}^{(s,J)} \, \beta_{ijk}^{(s,J)*} \tag{52}$$

When decomposing a Cartesian tensor T_{ijk}, symmetric in its last two indices, into its Cartesian irreducible terms $T_{ijk}^{(s,J)}$ one readily finds that one has two linearly independent terms of the first rank (J=1), a single term of the second rank (J=2) and a single term of

the third rank (J=3). Obviously, the third rank term $T^{(3)}_{ijk}$ equal in rank to the tensor T_{ijk} itself, is completely symmetric. Separation of two linearly independent first–rank terms is not unique. Here, we shall separate its the completely symmetric part

$$T^{(S,1)}_{ijk} = \frac{1}{15}\left[\delta_{ij}\left(2T_{nnk} + T_{knn}\right)\right.$$
$$\left. + \quad \delta_{ik}\left(2\,T_{nnj} + T_{jnn}\right) + \delta_{jk}\left(2\,T_{nni} + T_{inn}\right)\right] \qquad (53)$$

and the non–symmetric 'remainder':

$$T^{(N,1)}_{ijk} = \frac{1}{6}\left[\delta_{ij}\left(T_{nnk} - T_{knn}\right)\right.$$
$$\left. + \quad \delta_{ik}\left(T_{nnj} - T_{jnn}\right) - 2\,\delta_{jk}\left(T_{nni} - T_{inn}\right)\right] \qquad (54)$$

Clearly, the tensor $T_{ijk}^{(N,1)}$ is still symmetric in its last two indices, and so is the irreducible Cartesian second rank tensor $T_{ijk}^{(s,2)}$. Thus among the irreducible Cartesian tensors we are confronted with two possibilities with regard to their permutational symmetry:

(1) complete permutational symmetry–we denote this case by s=1

(2) symmetry in the last two indices–to be denoted by s=2

The autocorrelation function of the scattered radiation can now be written in the following form:

$$I_{\mathbf{n}}(t) \;=\; A^{2\,\omega} \sum_{s_1,s_2,J_1,J_2} \phi^0_{s_1 J_1 s_2 J_2}\; F^0_{s_1 J_1 s_2 J_2}(t) \tag{55}$$

as the sum of six terms, four of which are 'quadratic', $J_1 = J_2 = 1,\; s_1 = s_2 = 1; J_1 = J_2 = 1, s_1 = s_2 = 2; J_1 = J_2 = 2, s_1 = s_2 = 2; J_1 = J_2 = 3, s_1 = s_2 = 1$ and two mixed terms $J_1 = J_2 = 1, s_1 = 1, s_2 = 2$ and $J_1 = J_2 = 1, s_1 = 2, s_2 = 1$.

$$\phi^0_{1111} = \frac{1}{45}\left\{4\,(\mathbf{n}^*\cdot\mathbf{e})\,(\mathbf{n}\cdot\mathbf{e}^*) + (\mathbf{e}\cdot\mathbf{e})\,(\mathbf{e}^*\cdot\mathbf{e}^*)\right.$$
$$\left. + \;\; 2\,(\mathbf{n}^*\cdot\mathbf{e})\,(\mathbf{n}\cdot\mathbf{e})\,(\mathbf{e}^*\cdot\mathbf{e}^*) + 2\,(\mathbf{n}^*\cdot\mathbf{e}^*)\,(\mathbf{n}\cdot\mathbf{e}^*)\,(\mathbf{e}\cdot\mathbf{e})\right\} \tag{56}$$

$$F^0_{1111} = \frac{1}{15}\left\langle 4\beta_{iij}\,\bar{\beta}_{kkj} + 2\beta_{iij}\bar{\beta}_{jkk} + 2\,\beta_{ijj}\,\bar{\beta}_{kki} + \beta_{ijj}\,\beta_{ikk}\right\rangle \tag{57}$$

$$\phi^0_{1212} = \frac{1}{9}\left\{(\mathbf{n}^*\cdot\mathbf{e})\,(\mathbf{n}\cdot\mathbf{e}^*) + (\mathbf{e}\cdot\mathbf{e})\,(\mathbf{e}^*\cdot\mathbf{e}^*)\right.$$
$$\left. - \quad (\mathbf{n}^*\cdot\mathbf{e})\,(\mathbf{n}\cdot\mathbf{e})\,(\mathbf{e}^*\cdot\mathbf{e}^*) - (\mathbf{n}\cdot\mathbf{e}^*)\,(\mathbf{n}^*\cdot\mathbf{e}^*)\,(\mathbf{e}\cdot\mathbf{e})\right\} \tag{58}$$

$$F^0_{2121} = \frac{1}{3}\left\langle \beta_{iij}\,\bar{\beta}_{kkj} - \beta_{iij}\bar{\beta}_{jkk} - \beta_{ijj}\,\bar{\beta}_{kki} + \beta_{ijj}\,\bar{\beta}_{ikk}\right\rangle \tag{59}$$

$$\phi^0_{2111} = \frac{\sqrt{5}}{45} \left\{ (\mathbf{e}\cdot\mathbf{e})\,(\mathbf{e}^*\cdot\mathbf{e}^*) - 2\,(\mathbf{n}^*\cdot\mathbf{e})\,(\mathbf{n}\cdot\mathbf{e}^*) \right.$$
$$\left. + \quad 2\,(\mathbf{n}^*\cdot\mathbf{e})\,(\mathbf{n}\cdot\mathbf{e})\,(\mathbf{e}^*\cdot\mathbf{e}^*) - (\mathbf{n}^*\cdot\mathbf{e}^*)\,(\mathbf{n}\cdot\mathbf{e}^*)\,(\mathbf{e}\cdot\mathbf{e}) \right\} \tag{60}$$

$$F^0_{2111} = \frac{\sqrt{5}}{15} \left\langle \beta_{ijj}\,\bar{\beta}_{ikk} - \beta_{iij}\bar{\beta}_{jkk} + 2\,\beta_{ijj}\,\bar{\beta}_{kki} \right.$$
$$\left. - \quad 2\,\beta_{iij}\,\bar{\beta}_{kkj} \right\rangle \tag{61}$$

$$\phi^0_{1121} = \frac{\sqrt{5}}{45} \left\{ (\mathbf{e}\cdot\mathbf{e})\,(\mathbf{e}^*\cdot\mathbf{e}^*) \right.$$
$$- \quad 2\,(\mathbf{n}^*\cdot\mathbf{e})\,(\mathbf{n}\cdot\mathbf{e}^*) + 2\,(\mathbf{n}^*\cdot\mathbf{e}^*)\,(\mathbf{n}\cdot\mathbf{e}^*)\,(\mathbf{e}\cdot\mathbf{e})$$
$$- \quad \left. (\mathbf{n}^*\cdot\mathbf{e})\,(\mathbf{n}\cdot\mathbf{e})\,(\mathbf{e}^*\cdot\mathbf{e}^*) \right\} ** \tag{62}$$

$$F^0_{2111} = \frac{\sqrt{5}}{15} \left\langle \beta_{ijj}\,\bar{\beta}_{ikk} - \beta_{ijj}\bar{\beta}_{kki} + 2\,\beta_{iij}\,\bar{\beta}_{jkk} \right.$$
$$- \quad \left. 2\,\beta_{iij}\,\bar{\beta}_{kkj} \right\rangle \tag{63}$$

We note that $\phi^0_{2111} = (\phi^0_{1121})^*$ and $F^0_{2111} = (F^0_{1121})^*$.

$$\phi^0_{2222} = \frac{1}{15}\left\{2 - (\mathbf{n}^*\cdot\mathbf{e})(\mathbf{n}\cdot\mathbf{e}^*) - (\mathbf{e}\cdot\mathbf{e})(\mathbf{e}^*\cdot\mathbf{e}^*)\right.$$
$$- \quad 2(\mathbf{n}^*\cdot\mathbf{e}^*)(\mathbf{n}\cdot\mathbf{e}) + (\mathbf{n}^*\cdot\mathbf{e})(\mathbf{n}\cdot\mathbf{e})(\mathbf{e}^*\cdot\mathbf{e}^*)$$
$$\left. + \quad (\mathbf{n}^*\cdot\mathbf{e}^*)(\mathbf{n}\cdot\mathbf{e}^*)(\mathbf{e}\cdot\mathbf{e})\right\} \tag{64}$$

$$F^0_{2222} = \frac{1}{3}\left\langle 2\,\beta_{ijk}\,\bar{\beta}_{ijk} + \beta_{ijj}\,\bar{\beta}_{kki} + \beta_{iij}\bar{\beta}_{jkk}\right.$$
$$\left. - \quad 2\,\beta_{ijk}\,\bar{\beta}_{jik} - \beta_{ijj}\,\bar{\beta}_{ikk} - \beta_{iij}\,\bar{\beta}_{kkj}\right\rangle \tag{65}$$

$$\phi^0_{1313} = \frac{1}{105}\left\{5 - (\mathbf{e}\cdot\mathbf{e})(\mathbf{e}^*\cdot\mathbf{e}^*) + 10(\mathbf{n}^*\cdot\mathbf{e}^*)(\mathbf{n}\cdot\mathbf{e})\right.$$
$$- \quad 4(\mathbf{n}^*\cdot\mathbf{e})(\mathbf{n}\cdot\mathbf{e}^*) - 2(\mathbf{n}^*\cdot\mathbf{e})(\mathbf{n}\cdot\mathbf{e})(\mathbf{e}^*\cdot\mathbf{e}^*)$$
$$\left.- \quad 2(\mathbf{n}^*\cdot\mathbf{e}^*)(\mathbf{n}\cdot\mathbf{e}^*)(\mathbf{e}\cdot\mathbf{e})\right\} \tag{66}$$

$$F^0_{1313} = \frac{1}{15}\left\langle 5\,\beta_{ijk}\,\bar{\beta}_{ijk} + 10\,\beta_{ijk}\,\bar{\beta}_{jik}\right.$$
$$\left.- \quad 4\,\beta_{iij}\,\bar{\beta}_{kkj} - 2\,\beta_{iij}\bar{\beta}_{jkk} - 2\,\beta_{ijj}\,\bar{\beta}_{kki} - \beta_{ijj}\,\bar{\beta}_{ikk}\right\rangle \tag{67}$$

On the assumption that the hyperpolarizability tensor β_{ijk} is completely symmetric, the only non–zero molecular parameters will be $F^0_{1111}(t)$ and $F^0_{1313}(t)$.

$$F^0_{1111} = \frac{3}{5}\,\beta_{iij}\,\beta_{jkk} \tag{68}$$

$$F^0_{1313} = \beta_{ijk}\,\beta_{ijk} - \frac{3}{5}\,\beta_{iij}\,\beta_{jkk} \tag{69}$$

$$F^0_{1111} = \sum_M |B^1_M|^2 \tag{70}$$

$$F^0_{1313} = \sum_M |B^3_M|^2 \tag{71}$$

In particular, for the symmetry groups $\mathrm{C}_4 ... \mathrm{C}_\infty$ and $\mathrm{C}_{4V} ... \mathrm{C}_{\infty V}$, the totally symmetric tensor has the form $b_{333} = a; b_{311} = b_{131} = b_{113} = b_{322} = b_{232} = b_{223} = b$. Then for the molecular parameters we obtain:

$$F^0_{1111} = \frac{3}{5}(a + 2\,b) = |B^1_0|^2 \tag{72}$$

$$F^0_{1313} = \frac{2}{5}(a - 3\,b) = |B^3_0|^2 \tag{73}$$